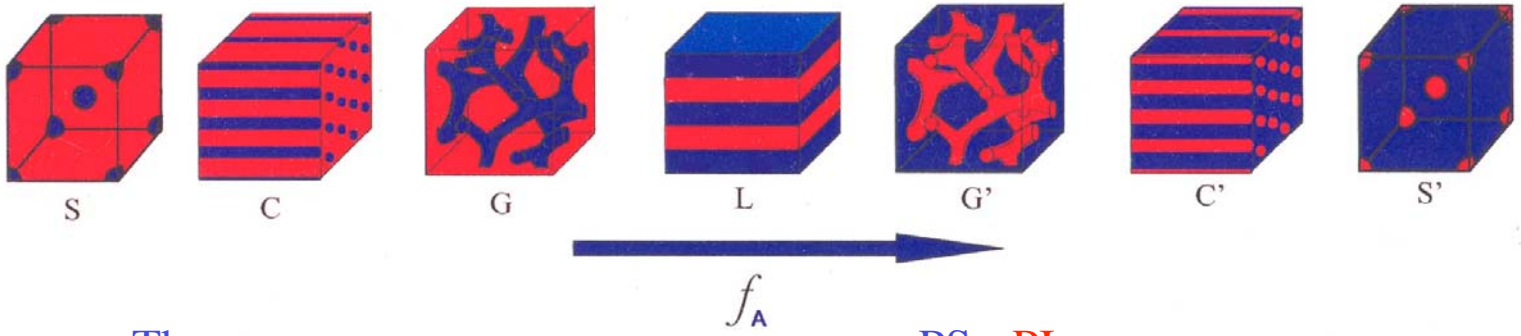
Georgia Institute of Technology
September 24, 2008

Membrane Dreams

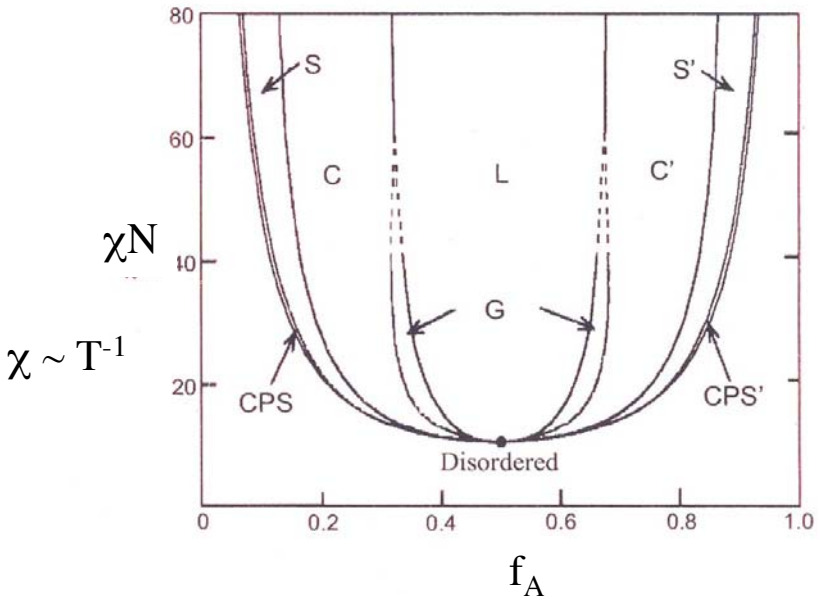
E. L. Cussler
University of Minnesota

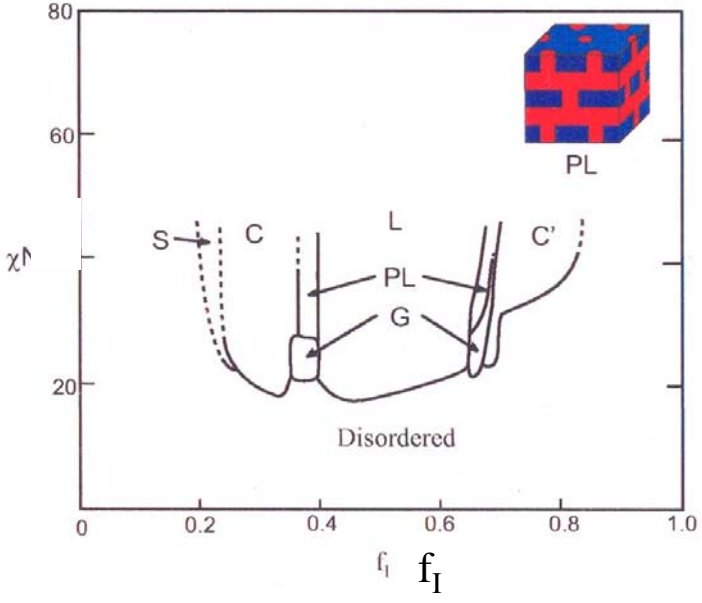
Dreams with Block Copolymers



Theory

PS - PI

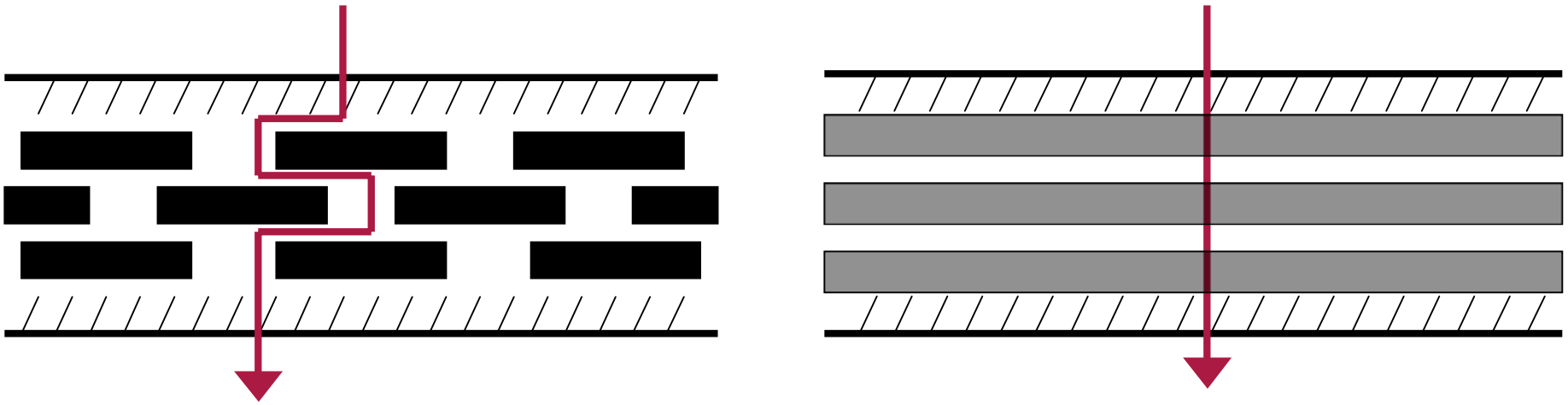




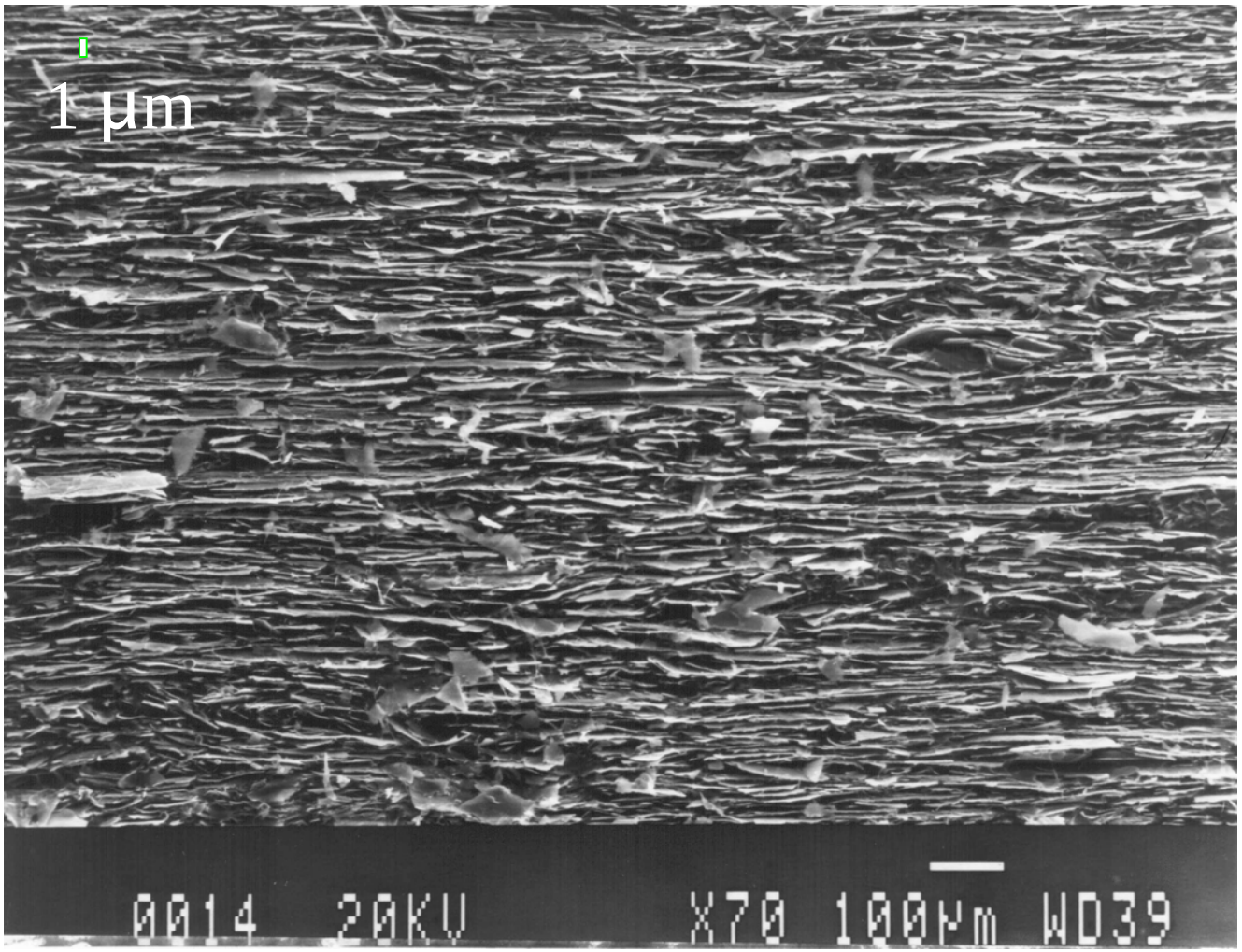
Three Membrane Dreams

1. Barriers
2. Nanopores
3. Ammonia Selective

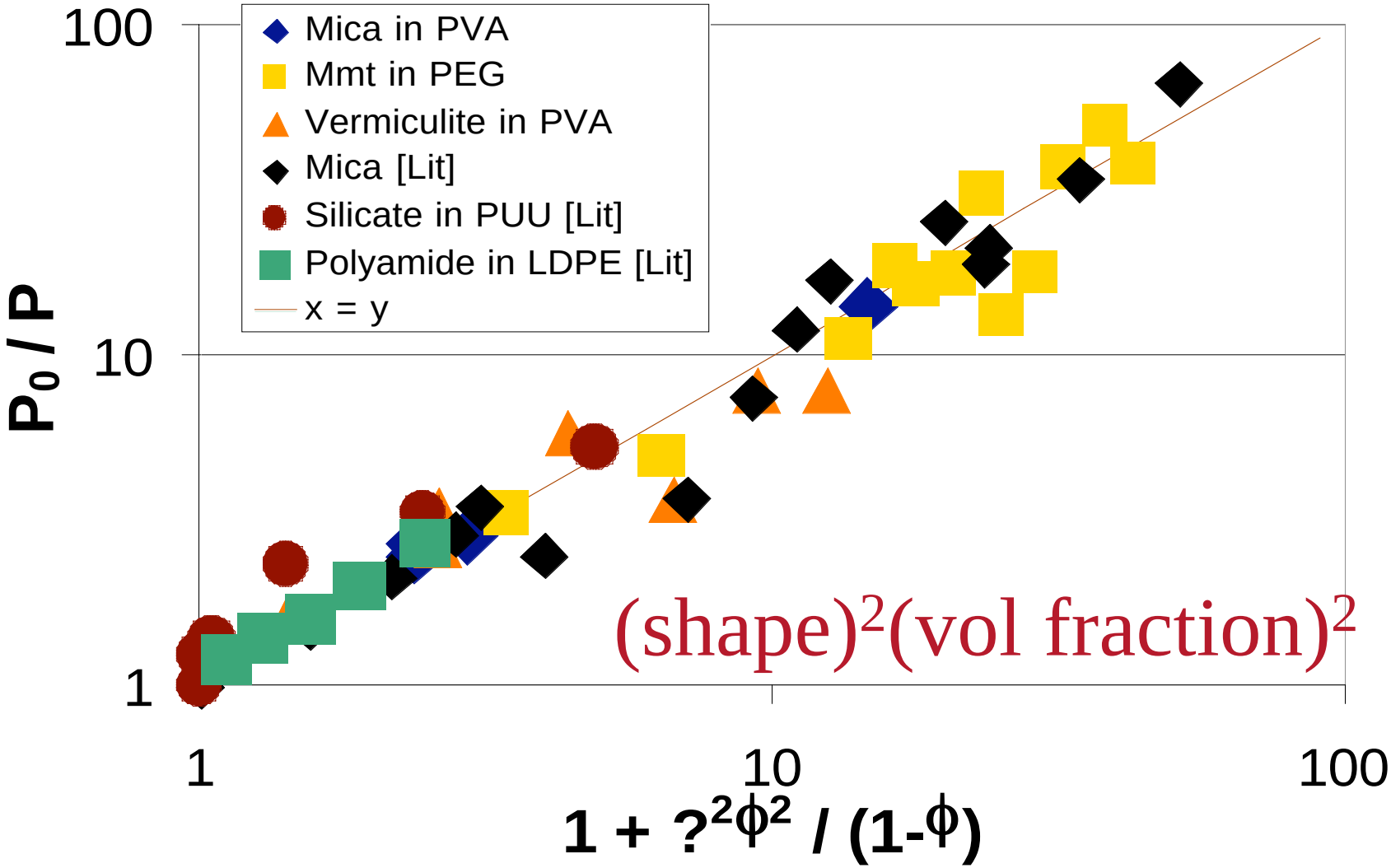
Original Dream: Reduce Permeability with Flakes



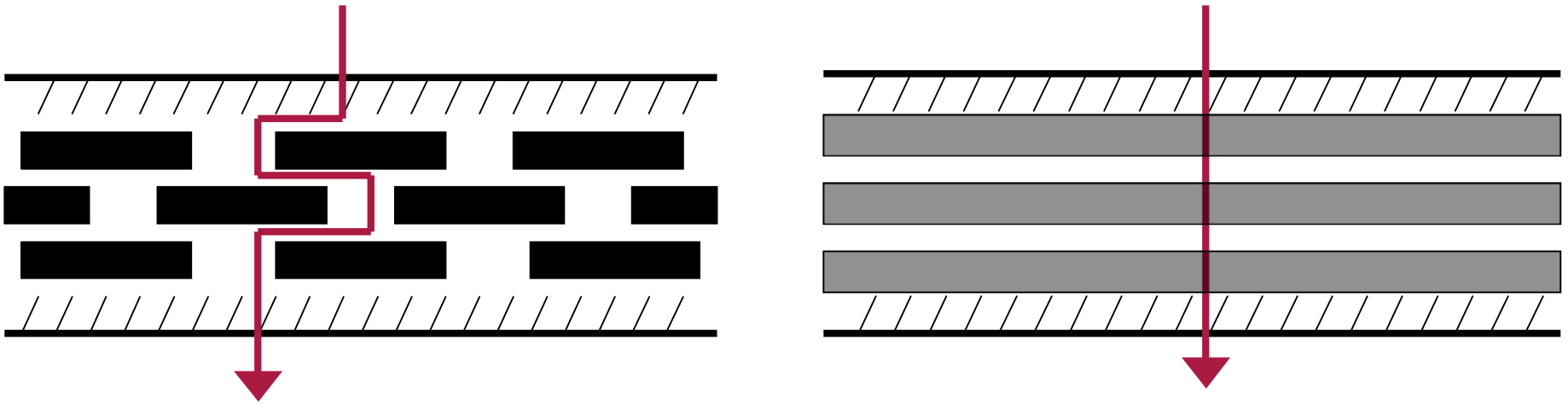
Flakes Reduce Permeability



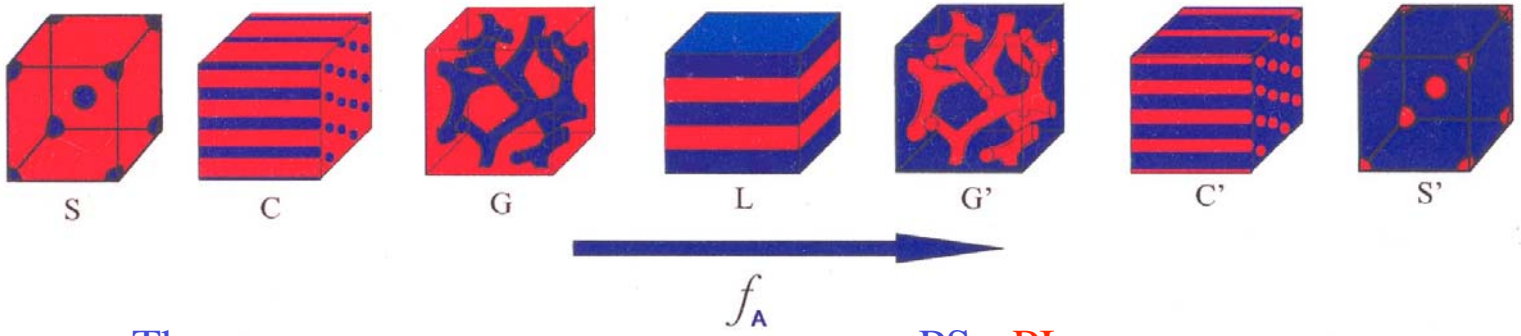
Flakes Reduce Permeability P



New Dream: Reduce Permeability with Lamellae

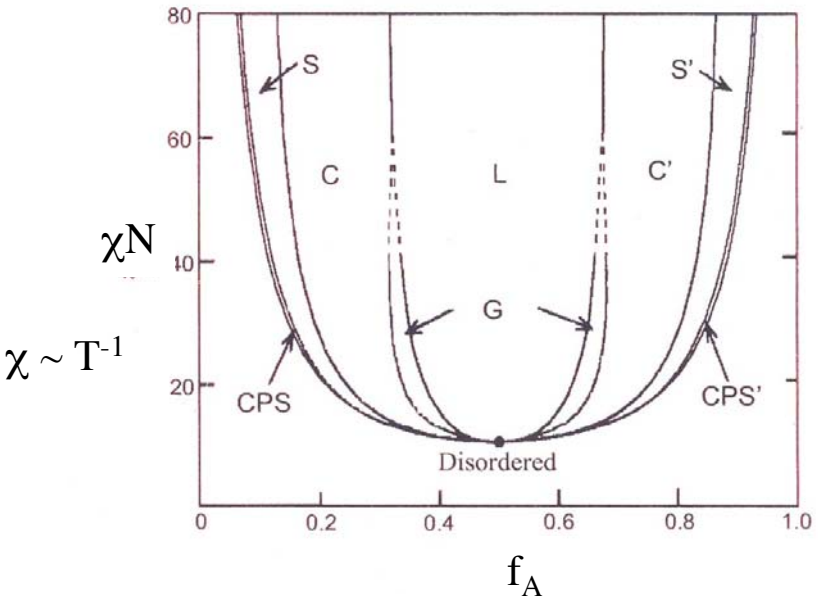


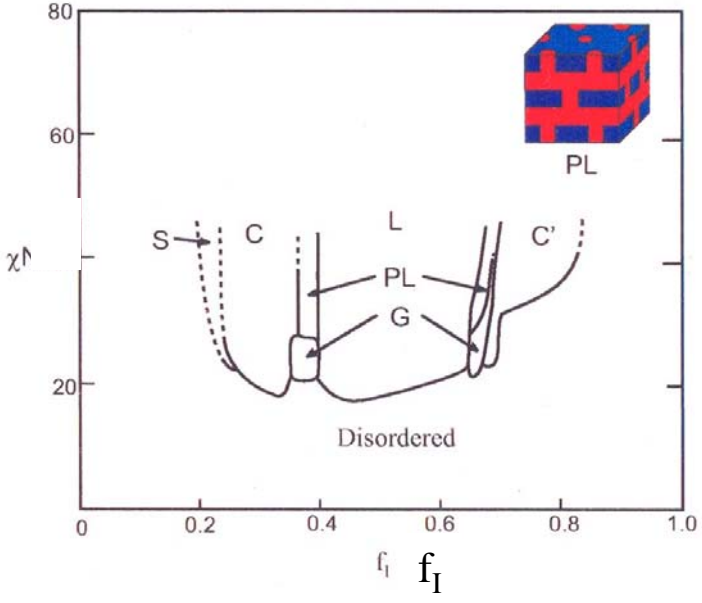
Self Assembled Lamellar Flakes



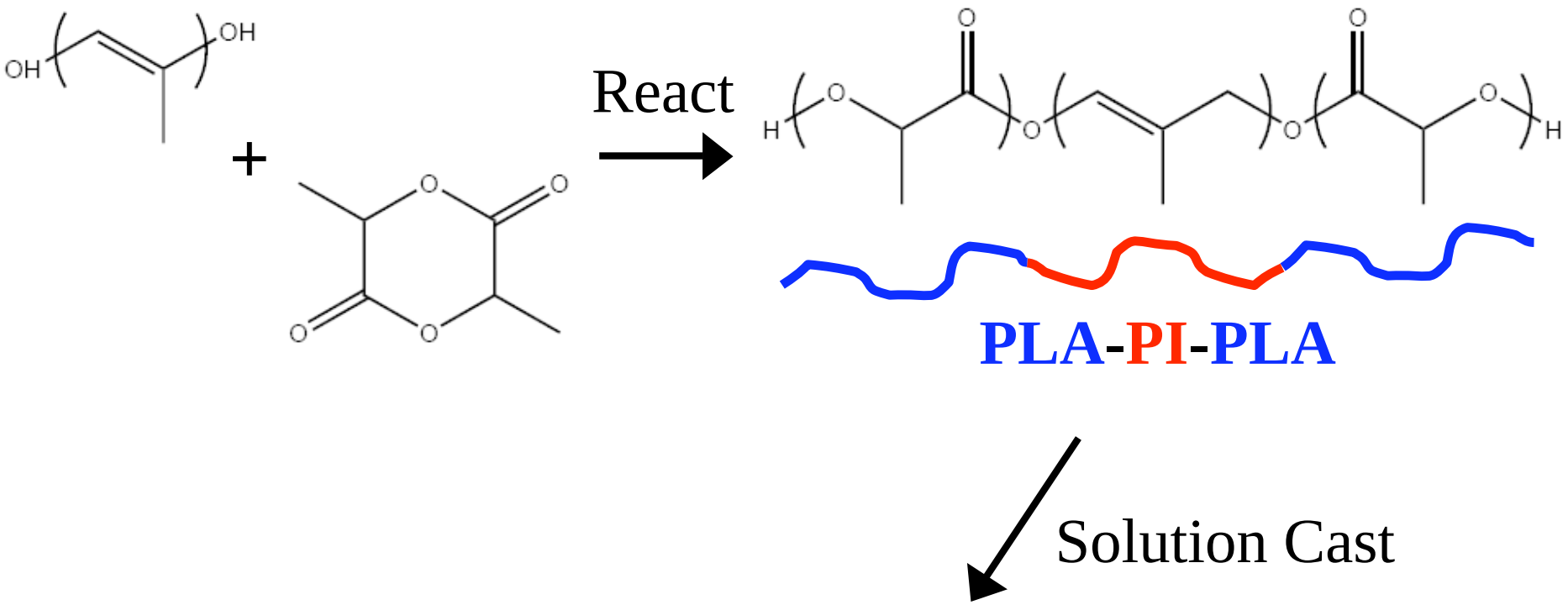
Theory

PS - PI

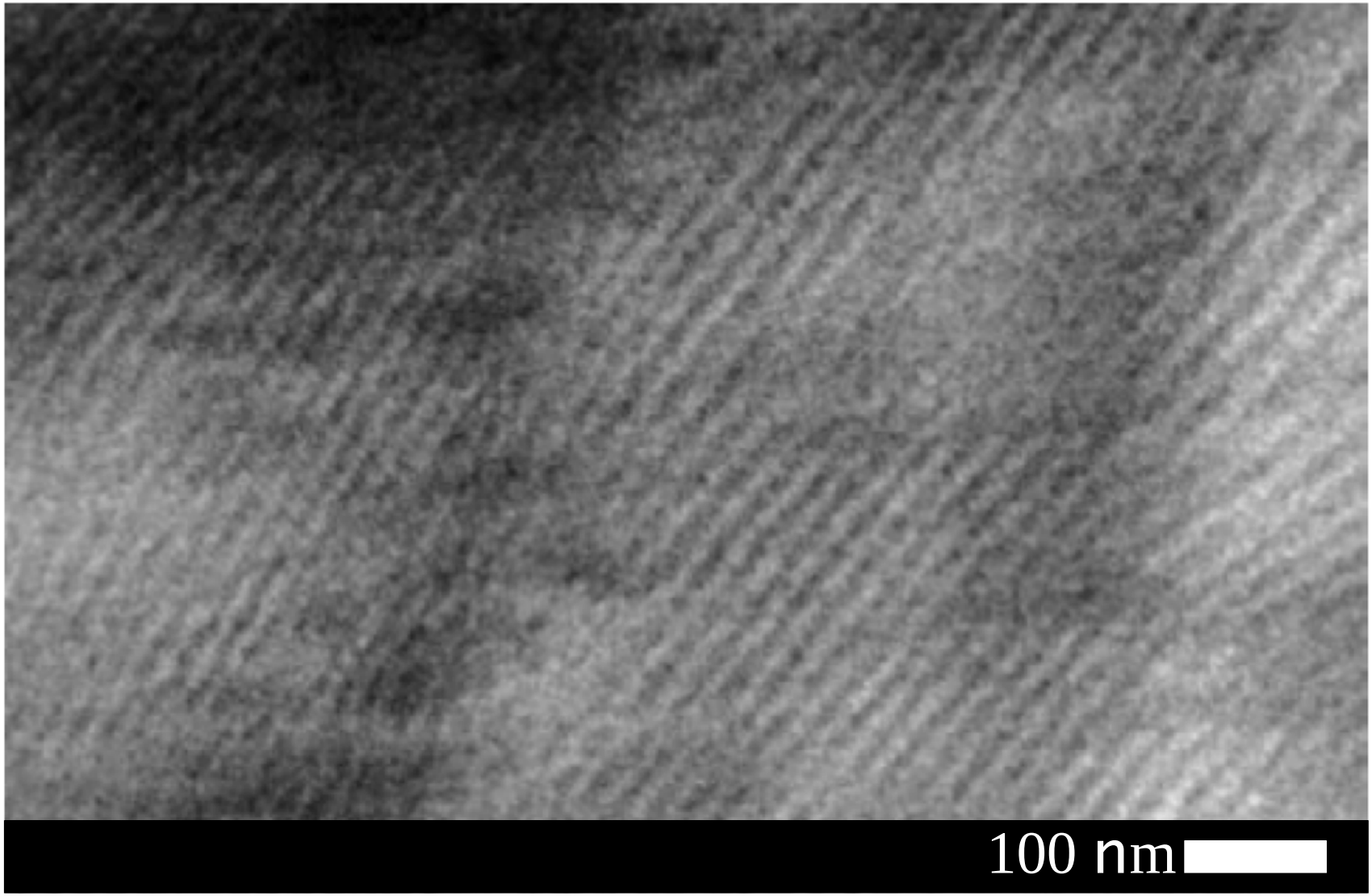




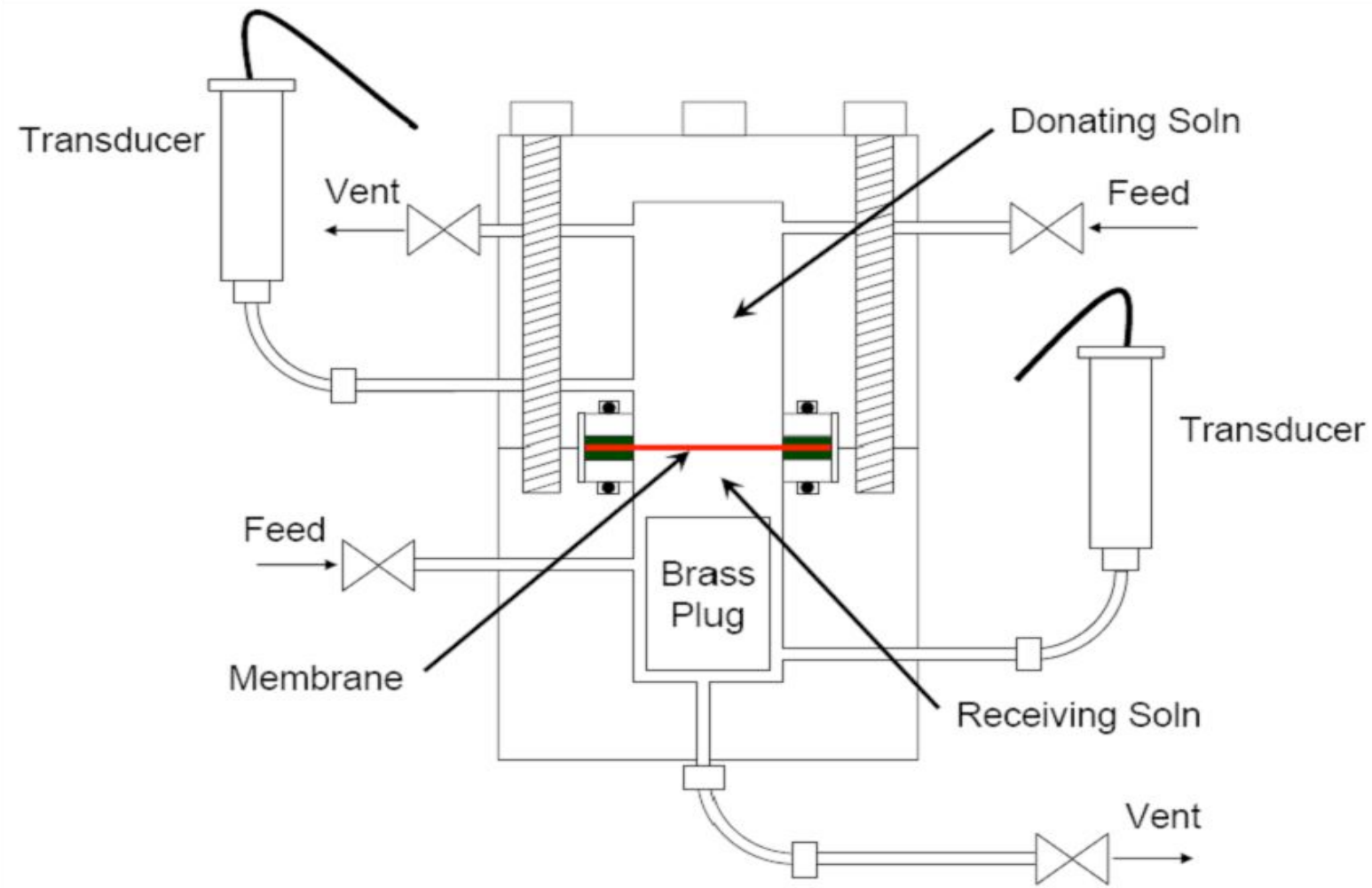
“Flakes” From Block Copolymers



Barrier with Aligned “Flakes”

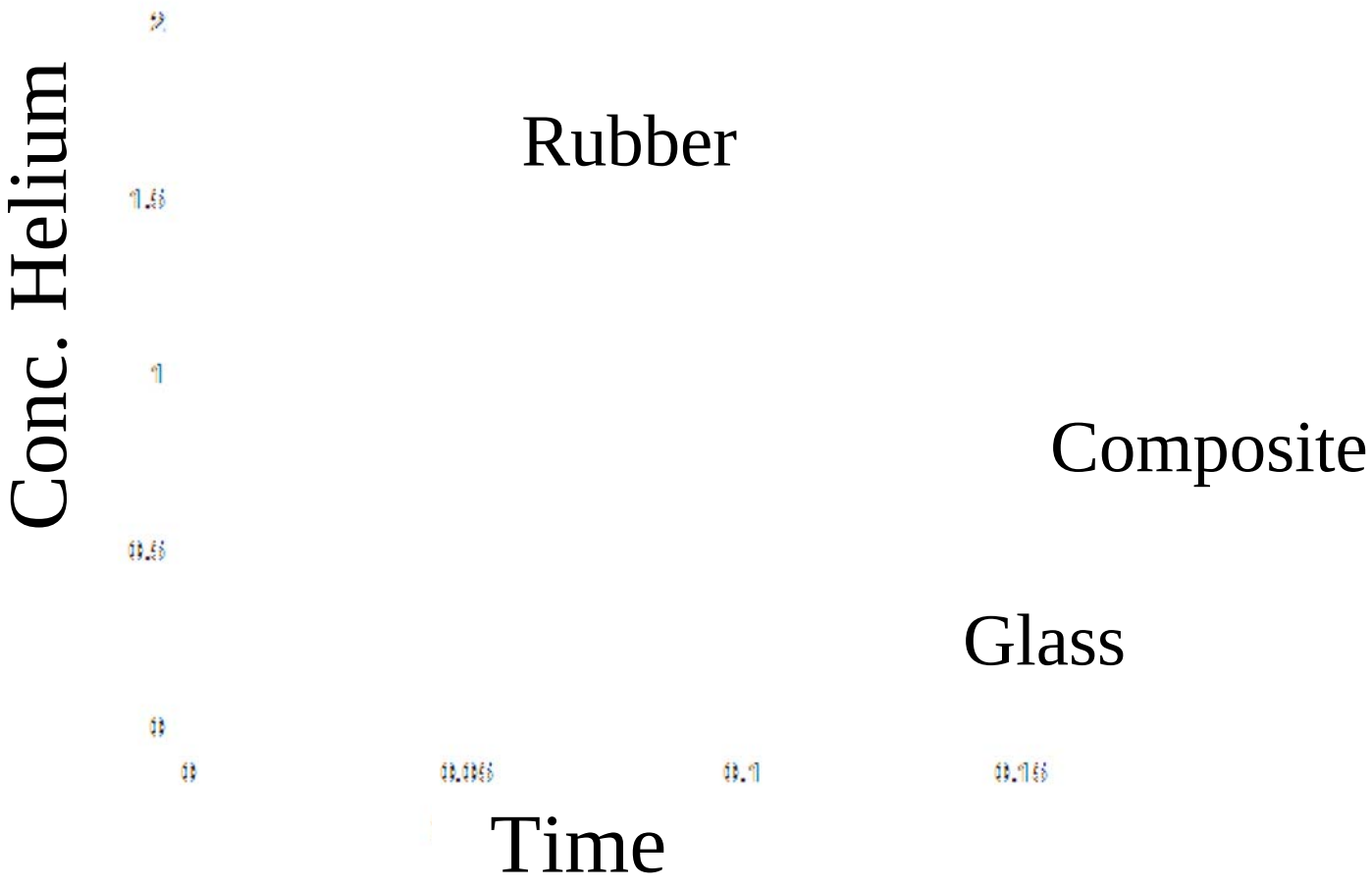


Basic Experiment: Gas Flux

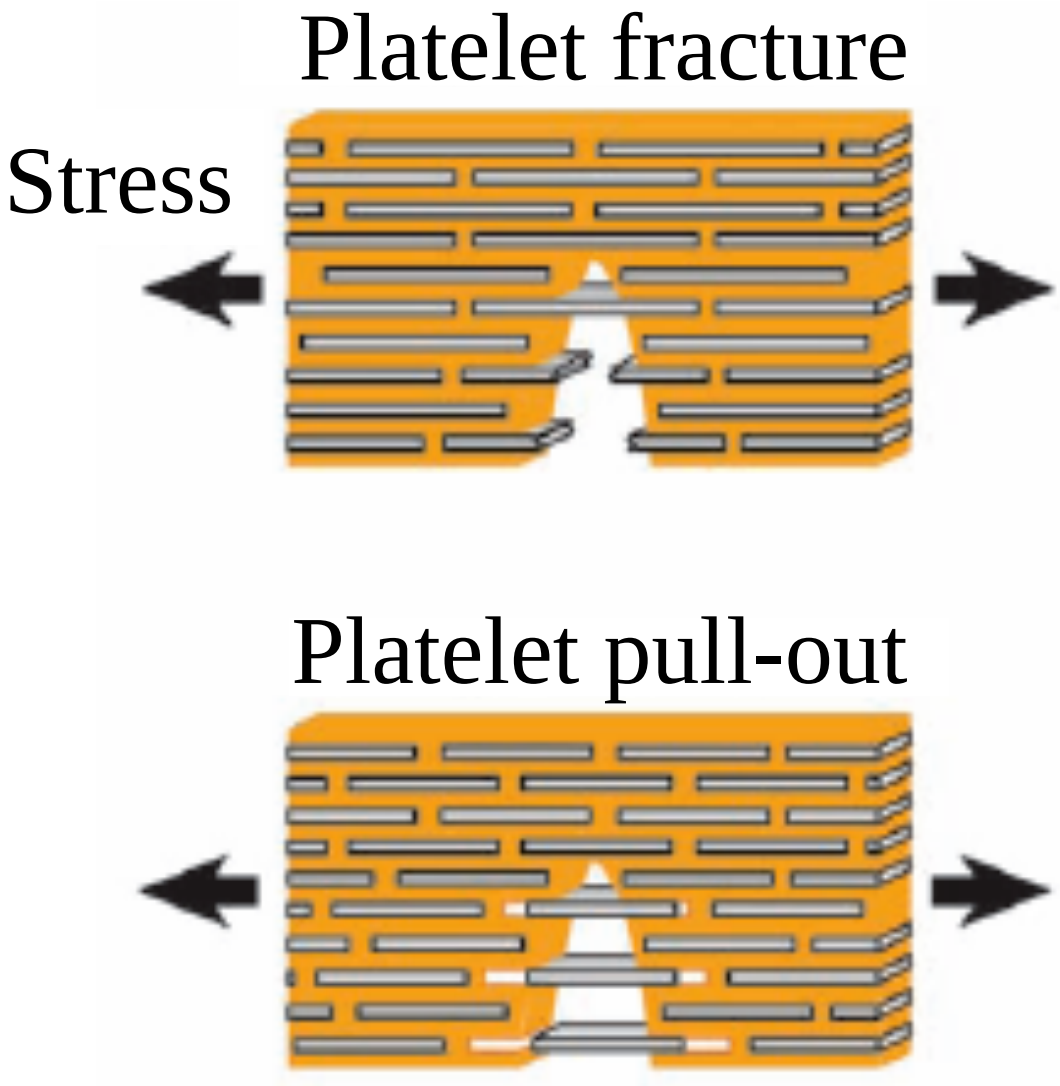


Self-Assembled Lamellae Work

$$\frac{1}{P} = \frac{1-\phi}{P_{Rubber}} + \frac{\phi}{P_{Glass}}$$



Lamellae Too Big, So Fracture



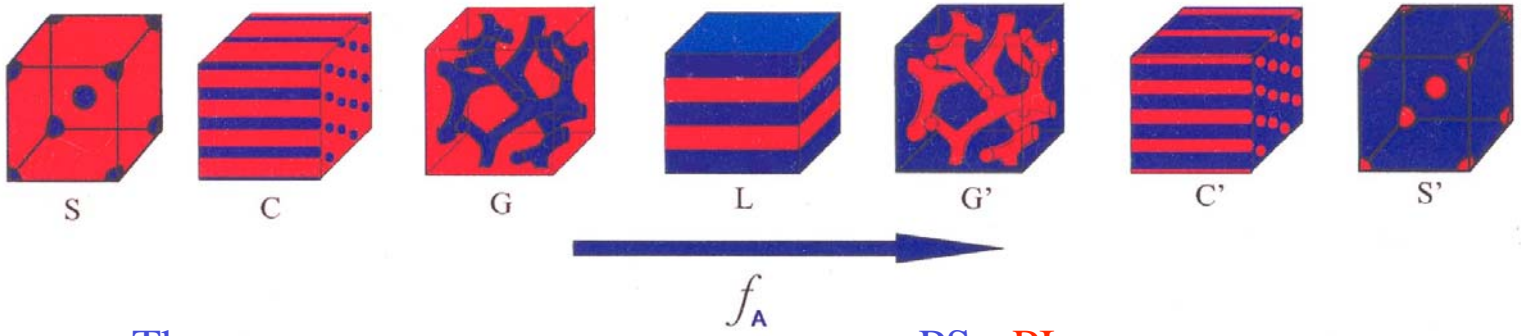
Bonderer, et. al., Science, (2008)

Three Membrane Dreams

1. Barriers from Lamellae…
   But Brittle
2. Nanopores

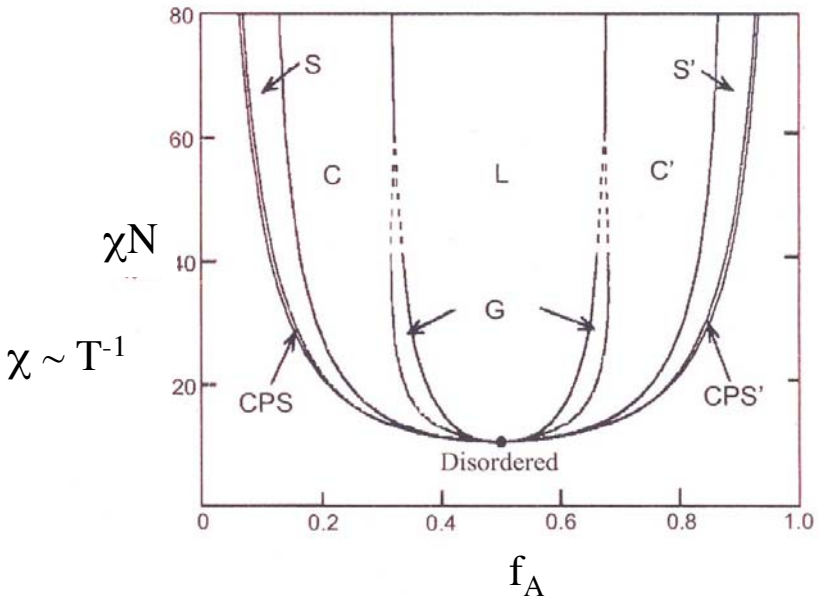
3. Ammonia Selective

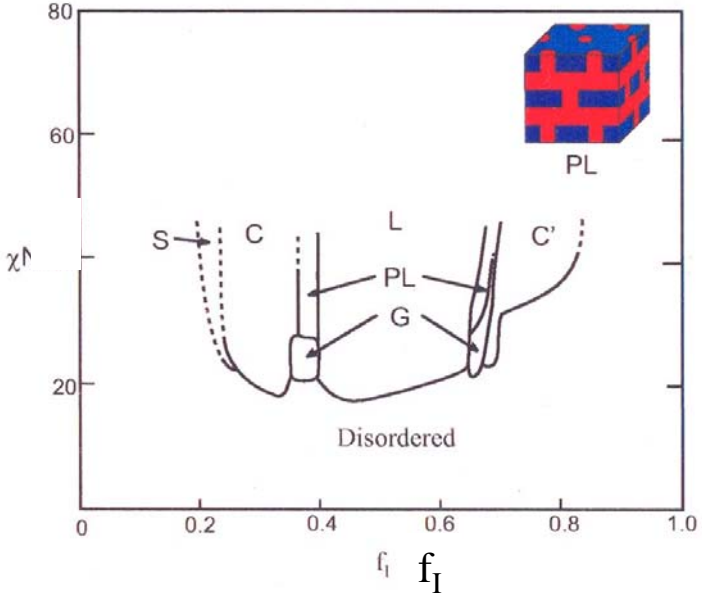
Two Routes for Nanopores: #1



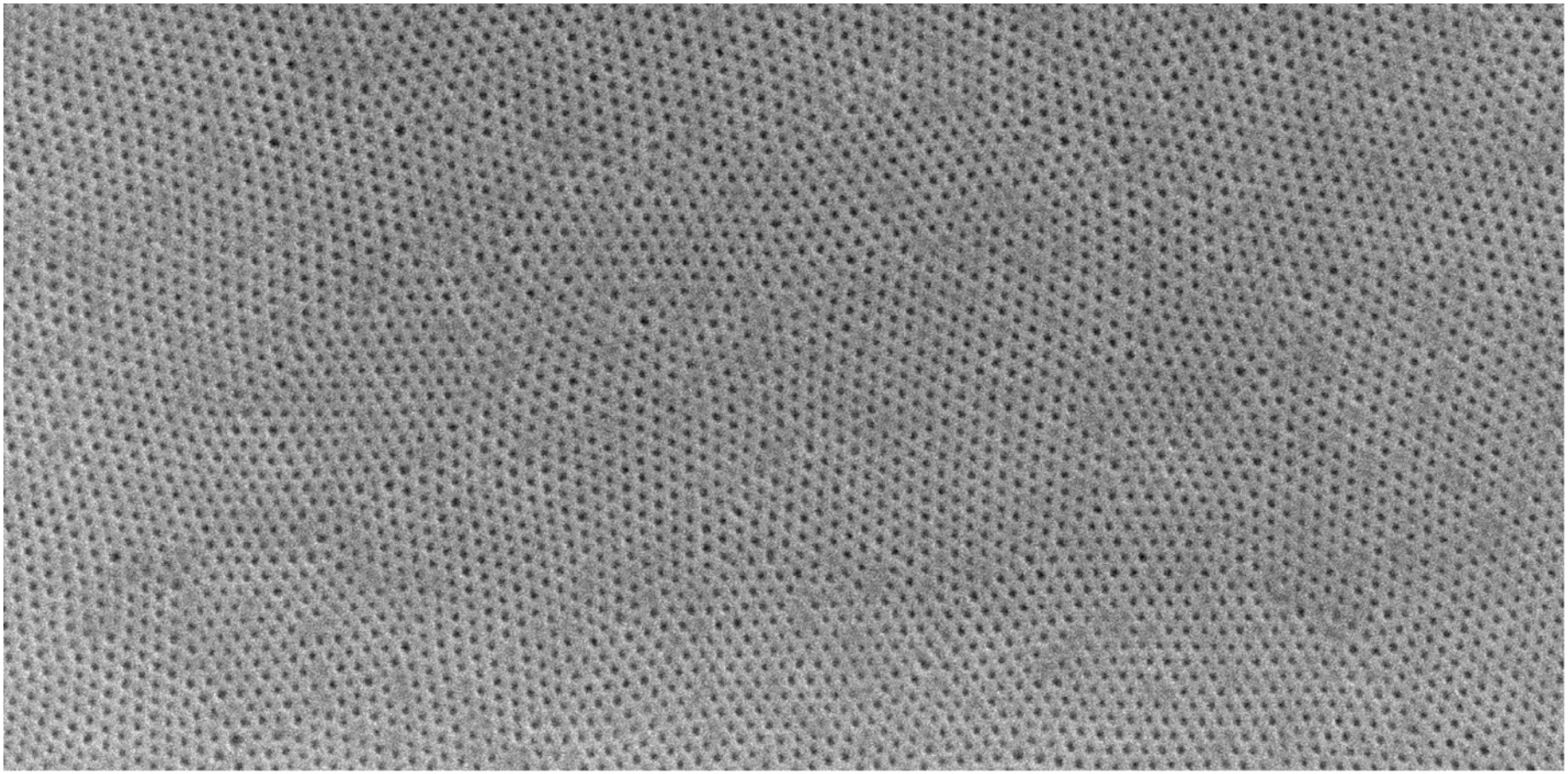
Theory

PS - PI



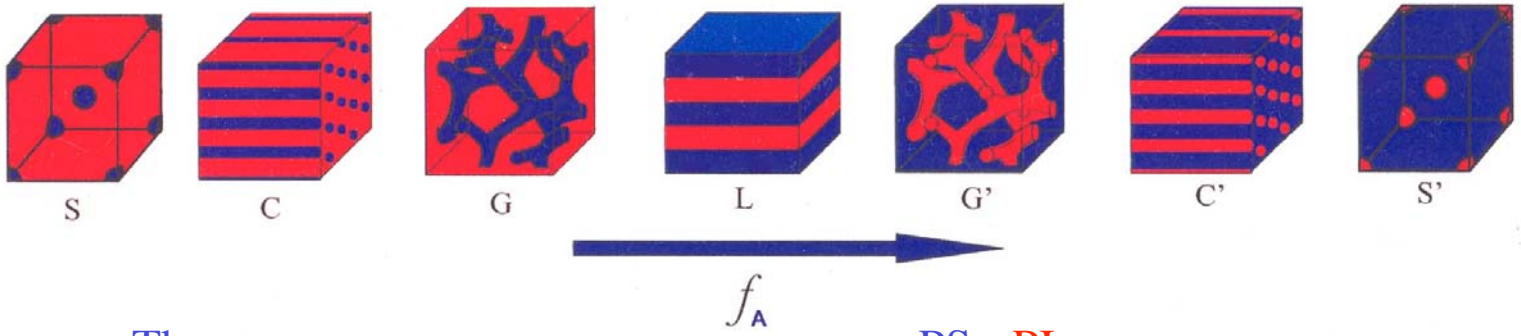


Route #1: Fast Evaporation



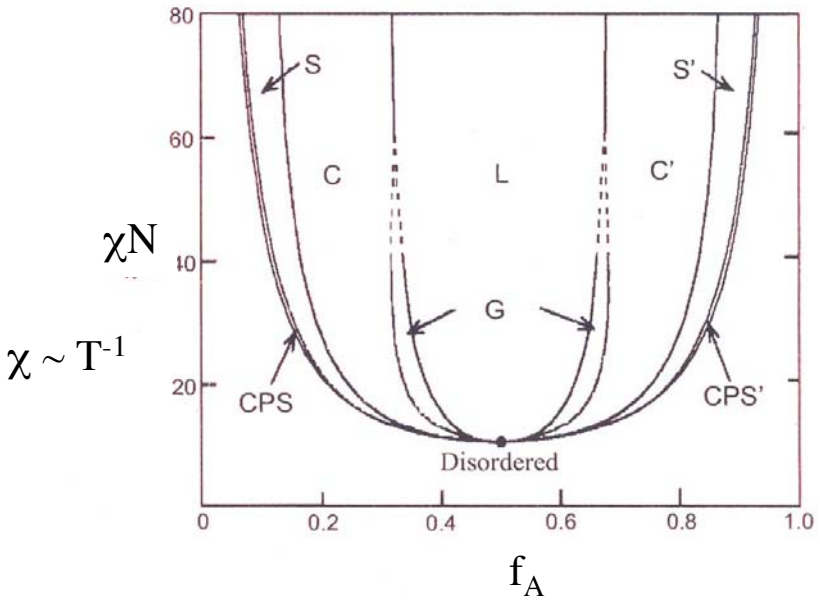
500nm

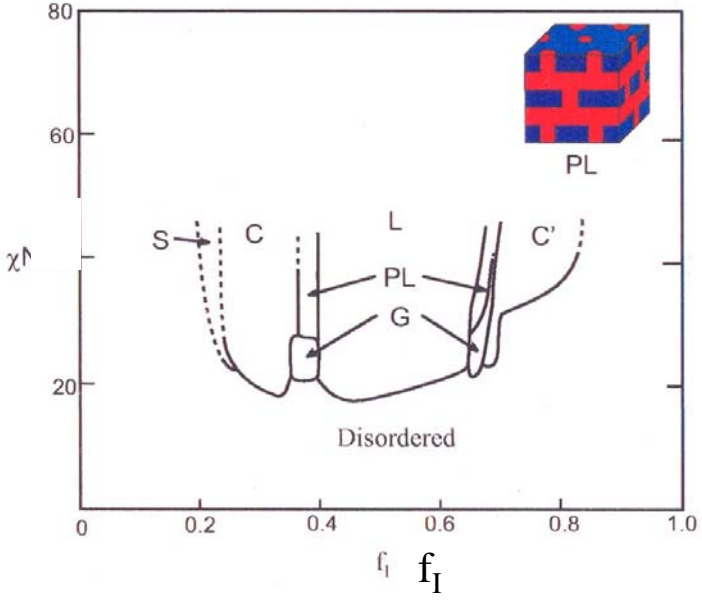
Two Routes for Nanopores: #2



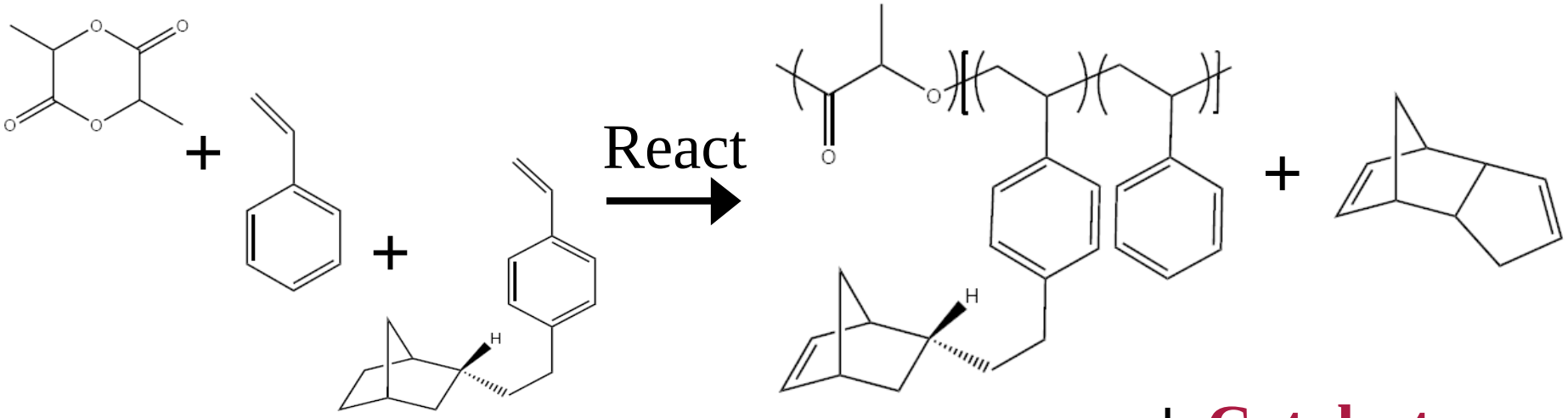
Theory

PS - PI



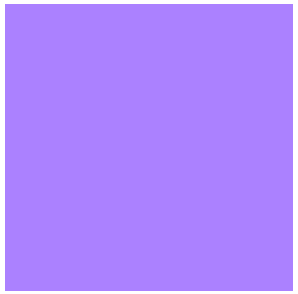


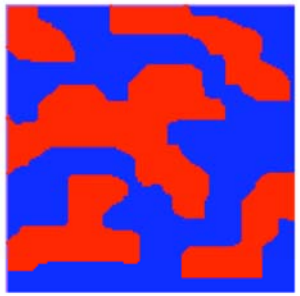
Route #2: Gyroid



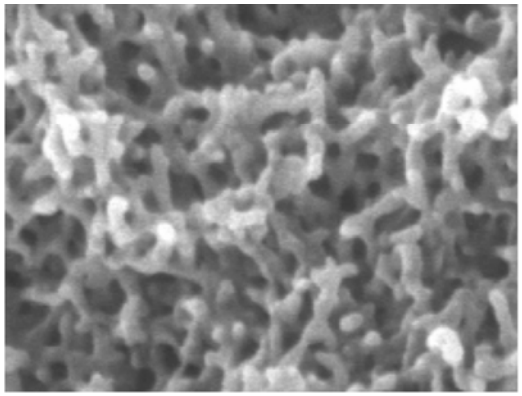
+ **Catalyst**

Solution Cast

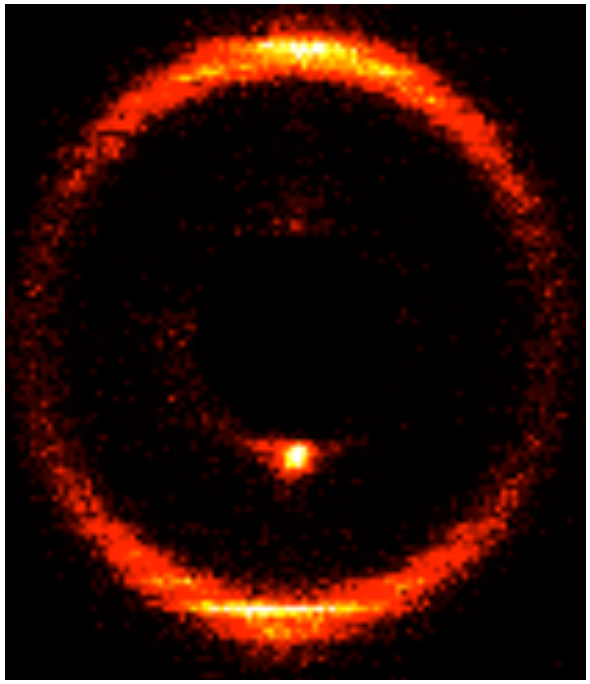


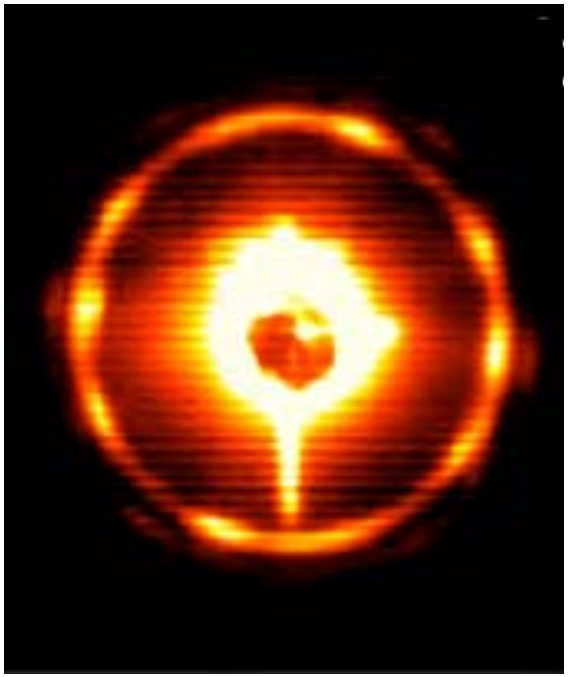


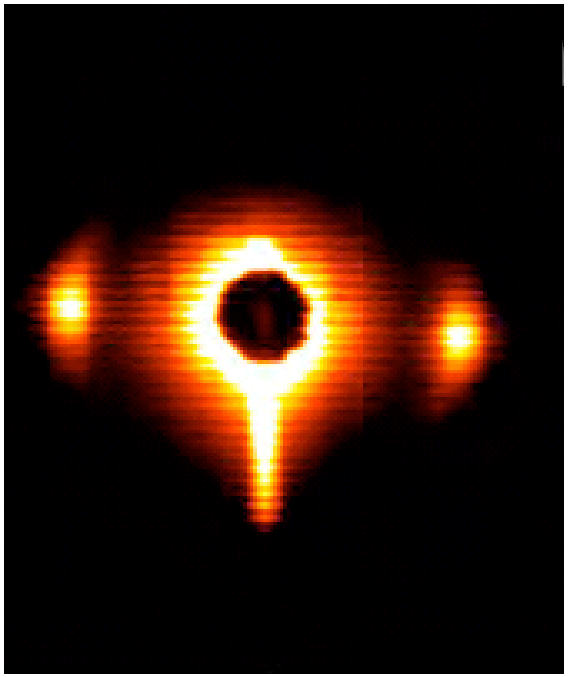
Etch



SAXS Patterns of Different Phases

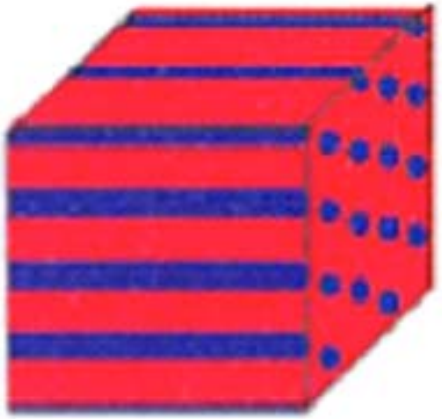






Lamellar

Gyroid



Cylinders

Pores Show Knudsen Diffusion

Block Copolymer: Pore Diameter 13.5 nm.

Solute	Permeance (Experimental)	Permeance (Knudsen)	Permeance (Kinetic Theory)
He	265.7	260.5	5815.7
Ar	84.2	82.2	633.9
N_2	100.4	98.3	702.0
O_2	89.4	92.0	713.4

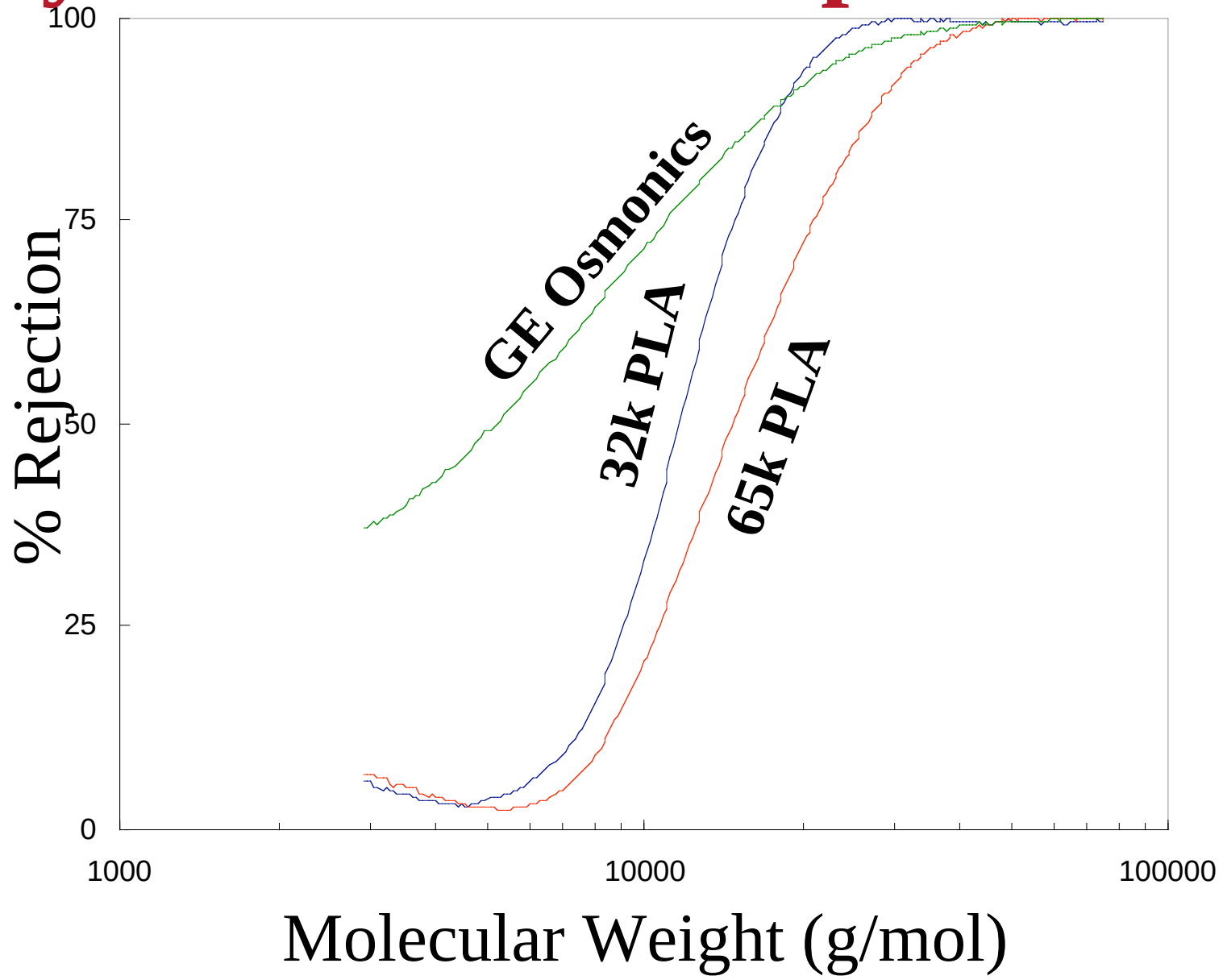
Track Etched: Pore Diameter 29.5 nm.

Solute	Permeance (Experimental)	Permeance (Knudsen)	Permeance (Kinetic Theory)
He	1.54	1.48	13.4
Ar	0.48	0.47	1.46

Gyroid Shows Similar Pores

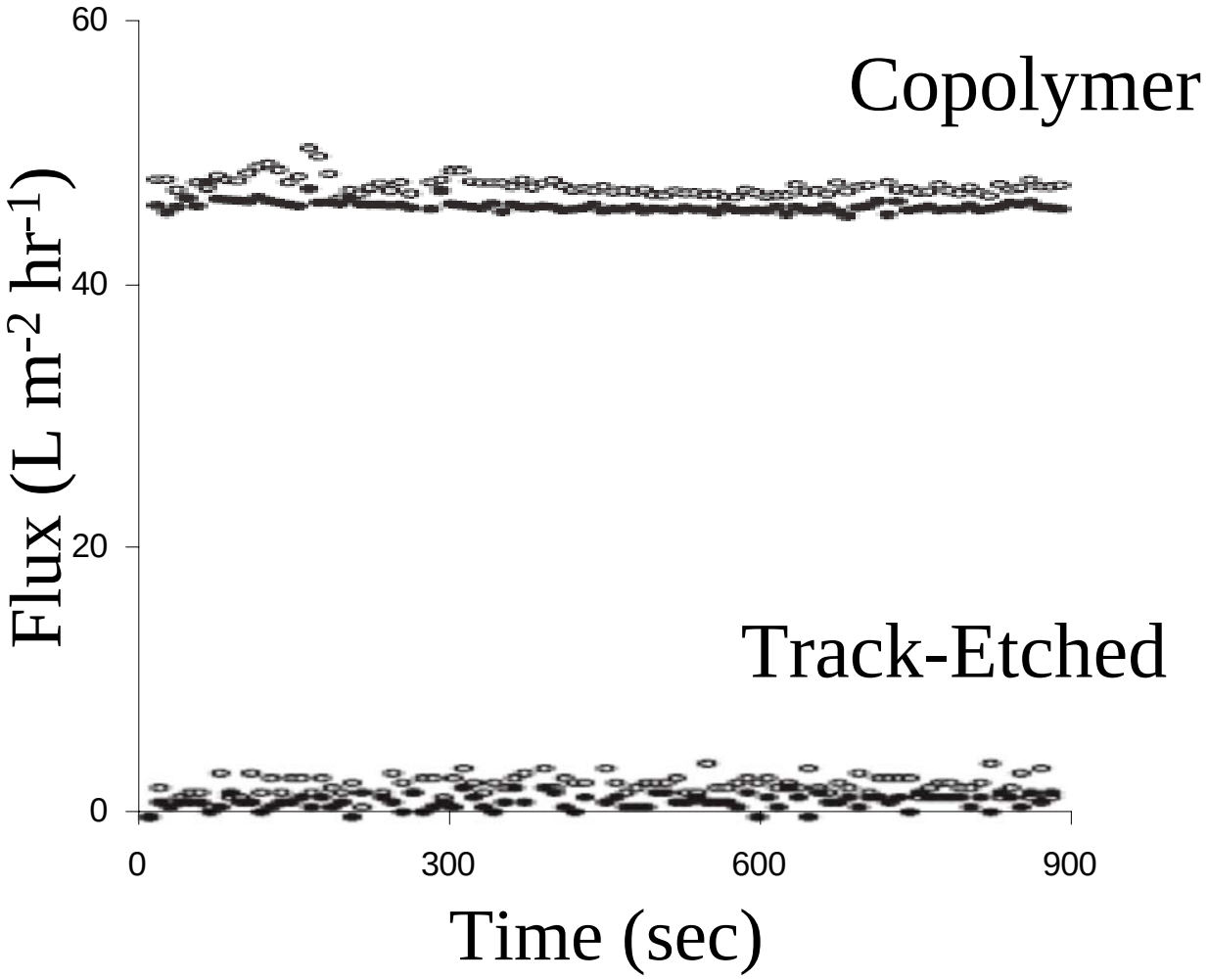
Method	diameter (nm)	tortuosity
Liquid Flow & Gas Diffusion	14.2	1.56
SAXS L	11.6	--
BET	15.1	--
SEM	20.0	--
Theory	--	1.54

Gyroid Shows Sharp MWCO



Pores Show Little Fouling

- **DI Water**
- **Solution w/ Virus**



Kim, et. al., Adv. Matls., (2006)

Three Membrane Dreams

1. Barriers From Lamellae

…but Brittle.

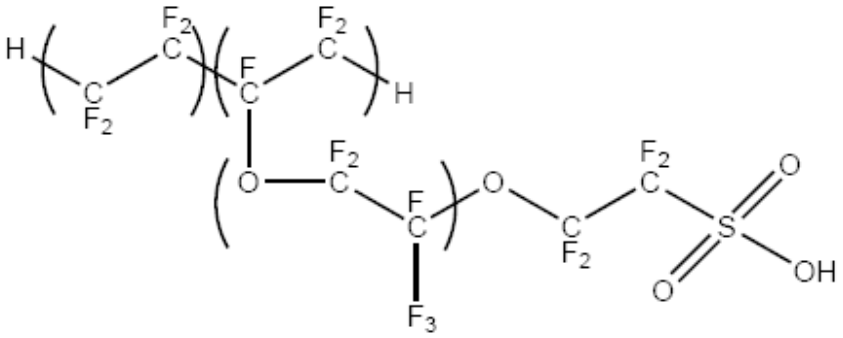
2.Nanopores 15 nm Monodisperse Pores

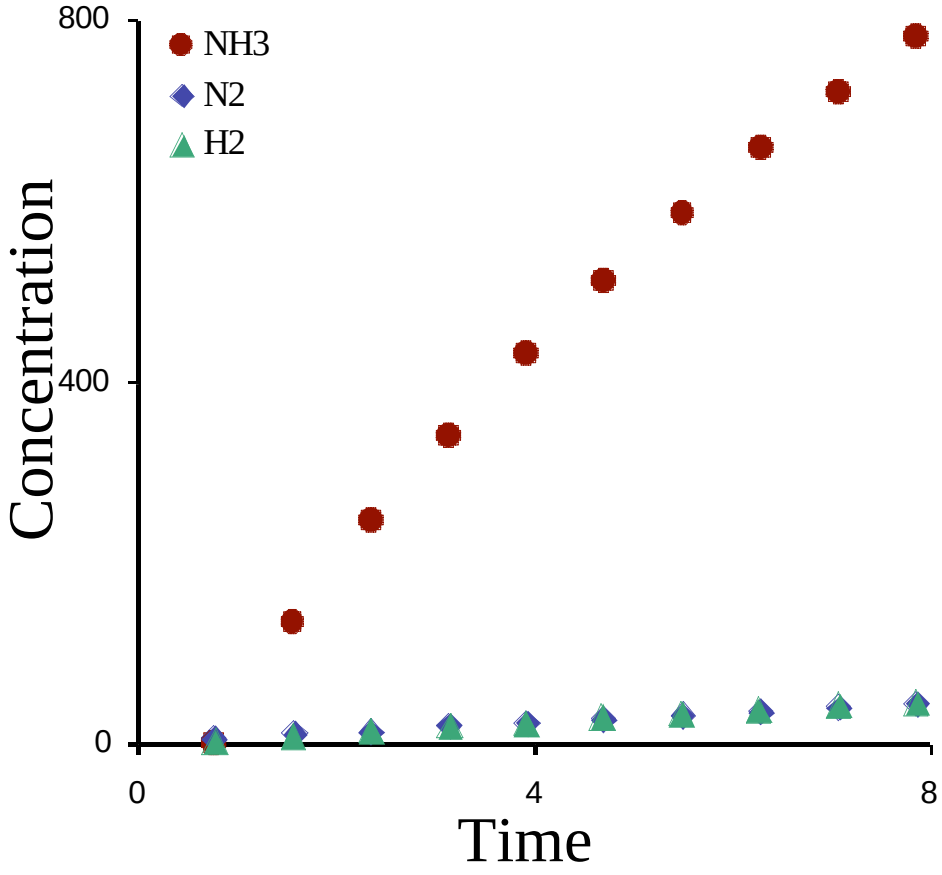
….but Fouling Unknown.

3.Ammonia

Single Gas Flux - Nafion

Chemical Structure

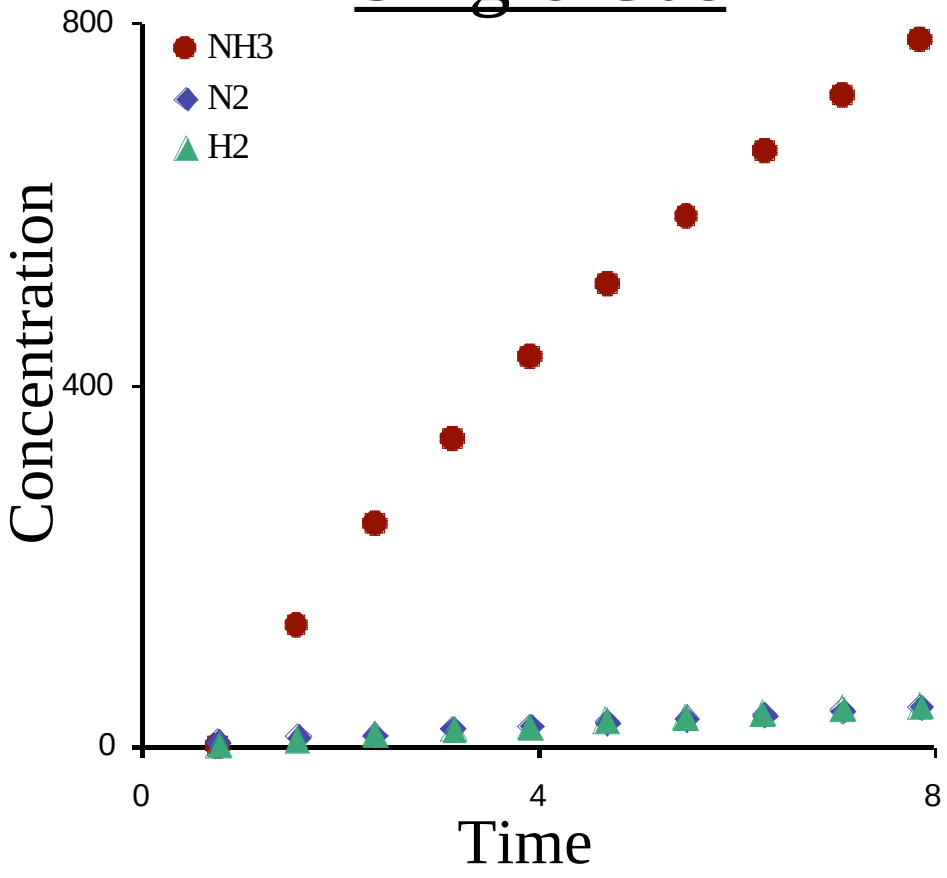




Ideal Selectivity (NH_3/N_2) > 200

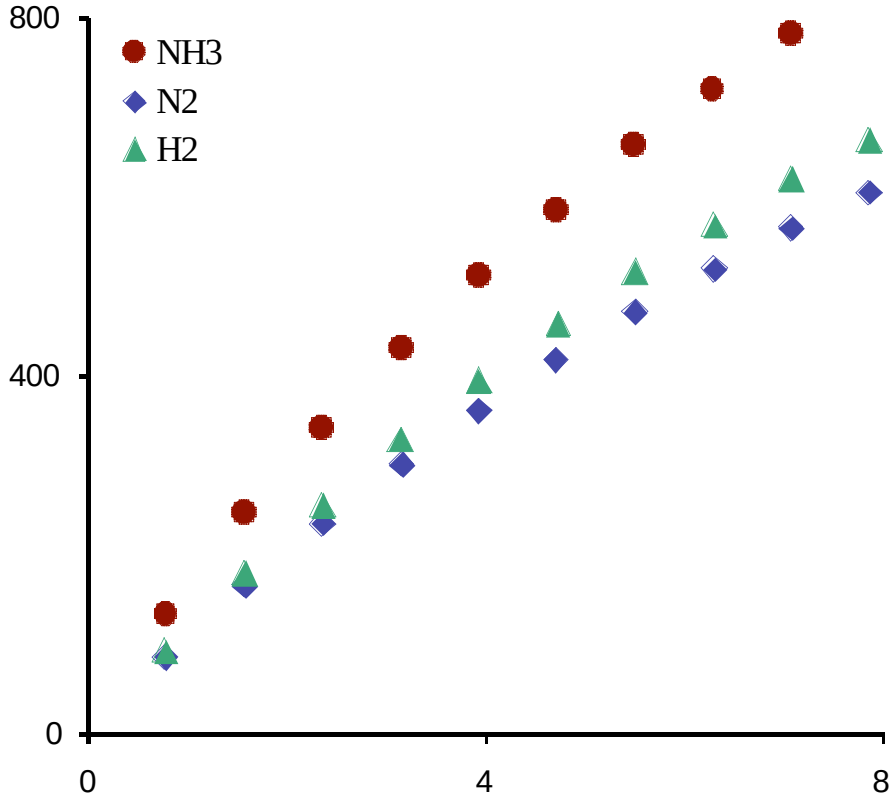
Nafion Loses Selectivity

Single Gas



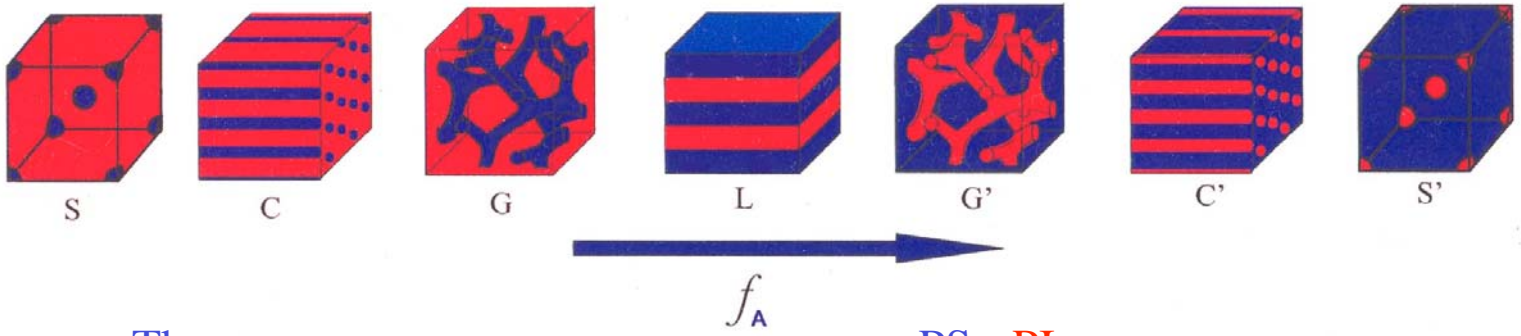
Selectivity (NH_3/N_2) > 200

Mixed Gases



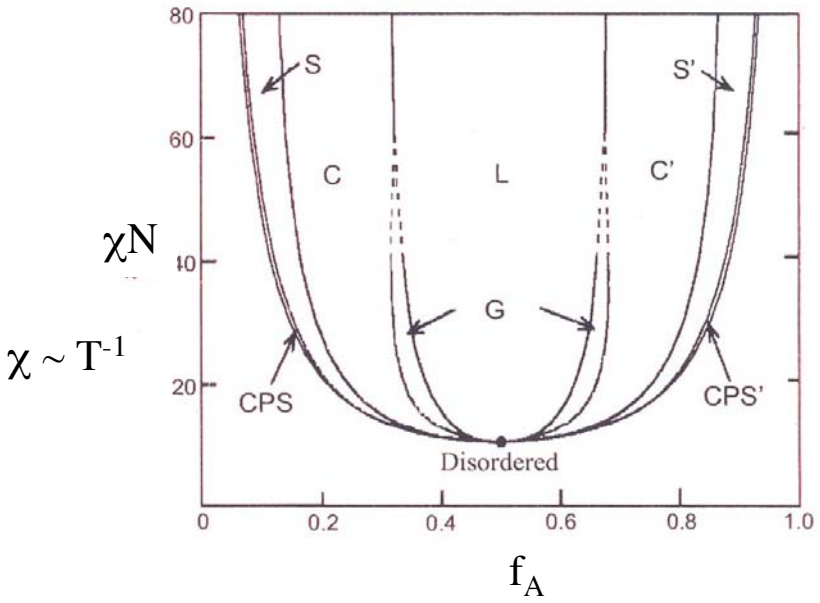
Selectivity (NH_3/N_2) ≈ 1.4

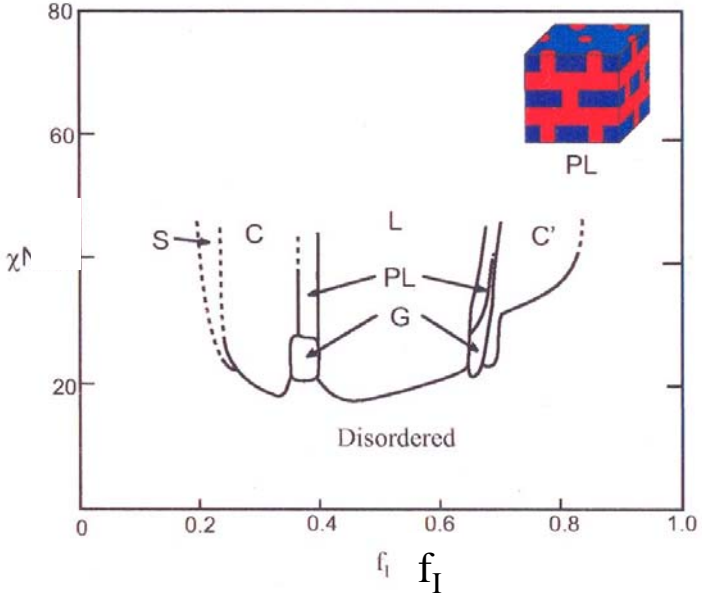
Self Assembled, Cross-Linked Gyroid



Theory

PS - PI

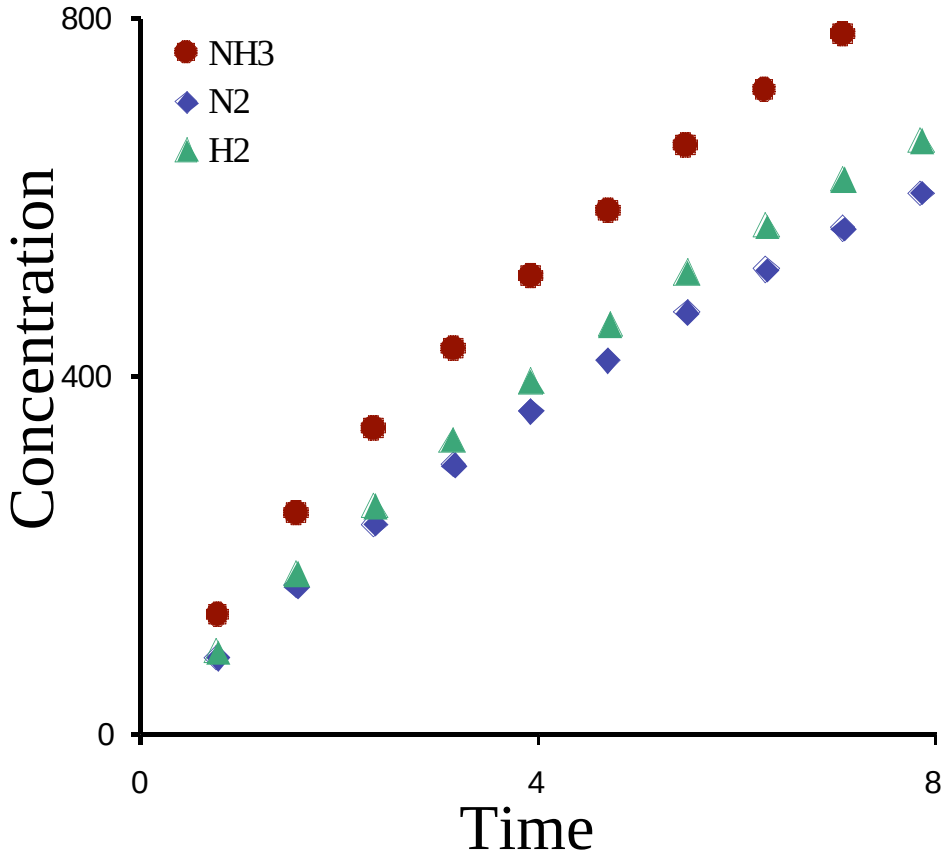




Sulfonated Copolymer Chemistry

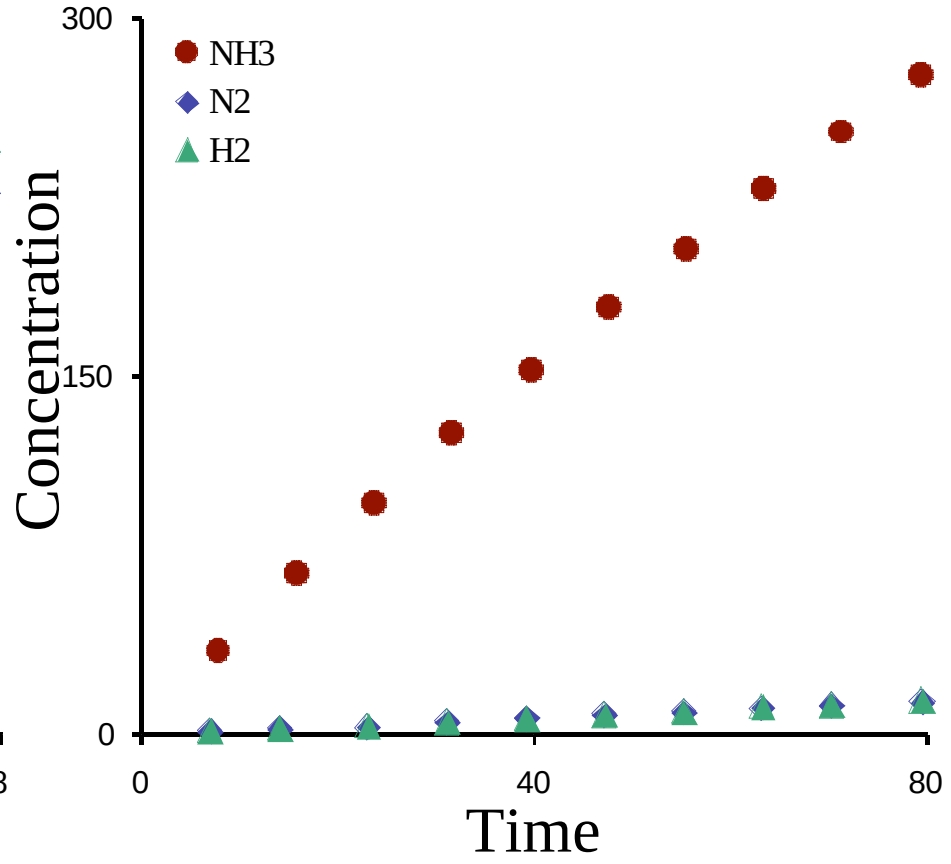
Copolymer Remains Selective

Nafion



Selectivity (NH_3/N_2) ≈ 1.4

Copolymer

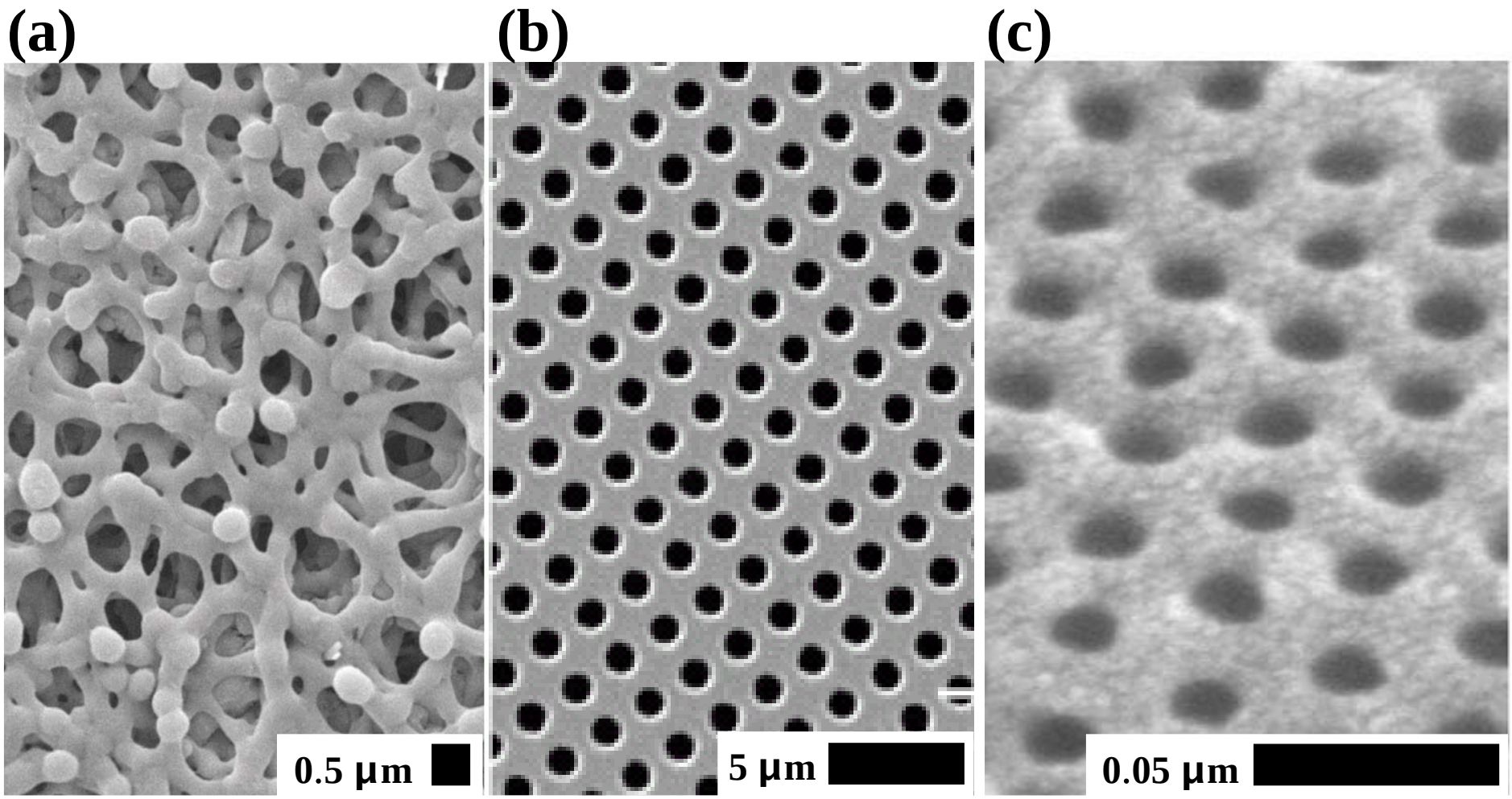


Selectivity (NH_3/N_2) > 100

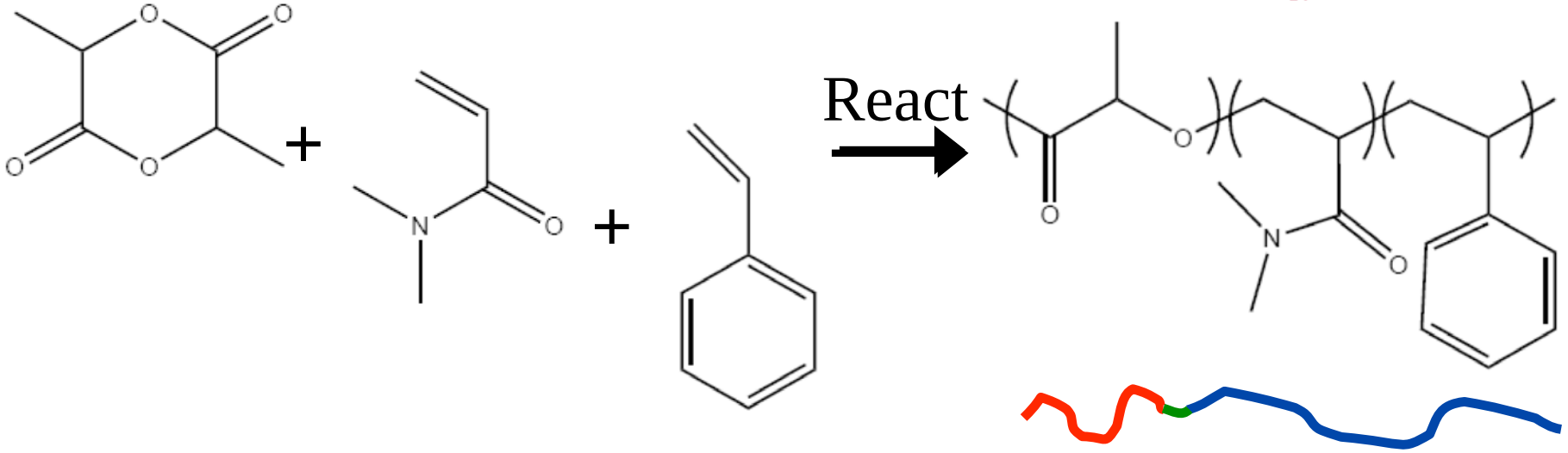
Dream Block Copolymers Give

1. Lamellar barriers… but they are fragile.
2. Monodisperse nanopores… but fouling is unknown.
3. Ammonia selective…at room temperature.

Three Size Selective Membranes

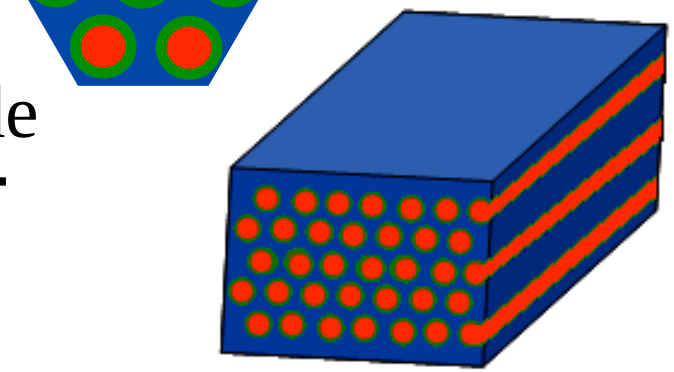


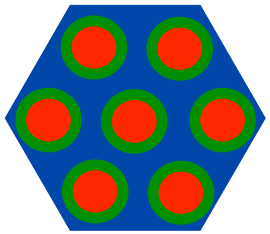
Porous Membrane Chemistry



PLA-PDMA-PS

Align





Degrade